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Multidimensional Gas Chromatography−Olfactometry for the Identification and Prioritization of Malodors from Confined Animal Feeding Operations

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Odor profiling efforts were directed at applying to high-density livestock operations some of the lessons learned in resolving past, highly diverse, odor-focused investigations in the consumer product industry. Solid-phase microextraction (SPME) was used for field air sampling of odorous air near and downwind of a beef cattle feedyard and a swine finisher barn in Texas. Multidimensional gas chromatography−olfactometry (MDGC-O) was utilized in an attempt to define and prioritize the basic building blocks of odor character associated with these livestock operations. Although scores of potential odorant volatiles have been previously identified in high-density livestock operations, the odor profile results developed herein suggest that only a very few of these may constitute the preponderance of the odor complaints associated with these environments. This appeared to be especially true for the case of increasing distance from both cattle feedyard and swine barn facilities, with *p*-cresol consistently taking on the dominant odor impact role with ever increasing distance. In contrast, at- or near-site odor profiles were shown to be much more complex, with many of the well-known lower tier odorant compounds rising in relative significance. For the cattle feedyard at- or near-site odor profiles, trimethylamine was shown to represent a significantly greater individual odor impact relative to the more often cited livestock odorants such as hydrogen sulfide, the organic sulfides, and volatile fatty acids. This study demonstrates that SPME combined with a MDGC-O−mass spectrometry system can be used for the sampling, identification, and prioritization of odors associated with livestock.

KEYWORDS: Odor; livestock; gas chromatography−olfactometry; solid-phase microextraction; multidimensional gas chromatography−mass spectrometry; volatile organic compounds; *p*-cresol

INTRODUCTION

Malodor characterization is among the most demanding of analytical challenges. This occurs because it is usually the case that aroma or odor critical components are present at very trace levels in a complex matrix of odor-insignificant volatiles (*1*). A large body of excellent analytical work has been reported during the past three decades relative to the volatile compounds emitted by high-density livestock operations. Scores of volatile compounds have been identified in these environments by utilizing various concentrating and analytical techniques (*2*−*7*). Included among these volatiles are a large number of compounds that are known to be potent individual odorants (*8*). Although as many as 411 compounds were reported and referenced in previous studies (*9*), relatively little is known about their overall odor impact and their impact on odor relative to the downwind distance. This is due to at least several challenges relative to these environments: (a) the variability between species, manure management systems, and animal production practices, (b) the variability and uncertainties associated with air/odor sampling and analysis methods, (c) the low concentrations of compounds that are known to be strong odorants, and (d) the apparent challenge to correlate chemical and olfactometry data.

The challenge relative to the odor issue is to extract from this large field of "potential" odorants the compounds that constitute the primary odor impact relative to livestock environments. Given sufficiently comprehensive and accurate reference and analytical data regarding the volatile compounds present

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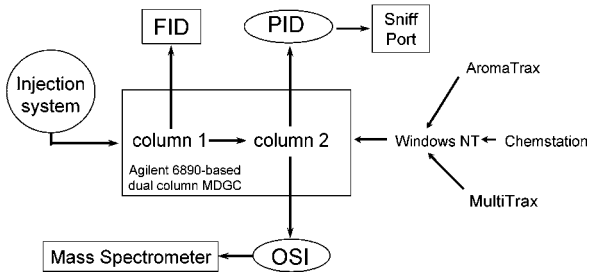

Figure 1. Schematic of AromaTrax MDGC–olfactometry system.

in these environments, it would seem to be possible to accurately predict and rank the primary odor impact compounds. However, from a practical standpoint, this does not produce satisfactory results in most cases. The factors working against such success are incomplete or imprecise odor threshold data in concert with the extremely low odor thresholds of many if not most of the key odorants present.

A practical alternative is to carry out gas chromtography−olfactometry (GC-O) based odor profile ranking studies relative to in situ headspace volatiles collections taken directly from the target environment (*1*, *7*, *10*, *11*). This is the approach that we routinely take in investigating odor issues surrounding matrices for which limited volatiles compositional data are available. The general experimental approach is to develop a detailed odorant ranking profile for a sensory graded "worst" case sample. Performing equivalent comparative odorant ranking profile analysis for equivalent sensory graded "best" case samples will typically indicate which of the "potential" odorants present in the field account for the odor character differences between the two samples.

The necessity of prioritizing the individual odor-carrying volatiles relative to a particular malodor issue in livestock odor focused investigations is needed to improve the knowledge of the sources of odor. Better understanding of key odorants and their fate in the environment is needed to address livestock odor issues. Over the past decade it has been our experience that such prioritization is essential to the resolution of the typical, crisis-driven malodor problems (*11*). Scores of these investigations have been successfully effected during this period, ranging from aroma and flavor complaints in foods and beverages to malodors in packaging, consumer products, and work environments.

In this paper, we demonstrate collaborative efforts undertaken with the Texas A&M—Texas Agricultural Experimental Station, Amarillo, and the West Texas A&M University, Canyon. These collaborations were directed at applying to high-density livestock operations some of the lessons learned in addressing these past, highly diverse odor focused investigations (*11*). In our past experience, odor profiling by GC-O has proven to be an essential element required for defining, prioritizing, and tracking the basic building blocks of odor character in complex matrices (*1*, *10*−*13*). The objective of this study was to demonstrate that this GC-O approach can be used for defining, prioritizing, and tracking livestock odorants in the air in and around swine and beef cattle operations.

MATERIALS AND METHODS

Multidimensional Gas Chromatography−Olfactometry−Mass Spectrometry (MDGC-O-MS) is a novel approach combining olfactometry and multidimensional GC separation techniques with conventional GC-MS instrumentation. An integrated AromaTrax system from Microanalytics (a MOCON Co.) of Round Rock, TX (**Figure 1**) was used for the reported GC-O profiling work. This integrated system utilizes the Agilent 6890 GC/5973 MS (Wilmington, DE) as the base platform. This basic GC-MS platform is then optimized for the odor profile application by the addition of multiple detectors (i.e., flame ionization, photoionization, and olfactometry); multiple columns [i.e., precolumn = 12 m × 0.53 mm i.d. BP5 × 1.0 μm from SGE (Austin, TX); analytical = 25 m × 0.53 mm i.d. BP20 × 1.0 μm from SGE]; MDGC capabilities (i.e., heart-cutting, cryogenic trapping, and backflushing); system automation and data acquisition software (i.e., MultiTrax ver. 6.00 and AromaTrax ver 6.00 from Microanalytics and ChemStation G1701BA ver. B.01.00 from Agilent). The general run parameters used during this project were as follows: injector, 240 °C; detectors FID 270 °C, PID 240 °C; column, 40 °C initial, 3 min hold, 7 °C/min, 220 °C final, 10 min hold; carrier gas, UHP-grade helium, constant pressure mode. The heart-cut valve between the precolumn and analytical column was open between 0.05 and 35 min. Backflush of the precolumn was activated between 36 and 40 min.

For odor profile investigations the critical elements of the AromaTrax GC-O system are the following (**Figure 1**):

- An olfactory detector enables the analyst to apply an odor tag to a peak or a region of the chromatographic separation. The odor tag consists of editable odor character descriptors, an odor event time span, and perceived odor intensity.
- A high-sensitivity electronic signal (i.e., PID detector in series) and MSD compound identification (i.e., MSD in parallel) are required, as is simultaneous olfactory response.
- A dual-column MDGC system with heart-cutting capability enables isolation of critical trace level odorants from complex background matrices (*1*, *10*, *12*, *13*). In such a dual-column system, heart-cutting is a mechanical separation process in which, to enhance resolution, a small "region of interest" from the first column separation is diverted to a second column, representing different phase selectivity. A cryotrap acting at the front of the analytical column further enhances these "needle from the haystack" separations by enabling transferred heart-cut segments to be refocused prior to final separation on the analytical column and delivery to the PID-MS-O detector system.
- AromaTrax software facilitates the olfactory event note-keeping for the analyst (i.e., human "olfactory detector"). Utilizing a touch-screen monitor, the analyst records the appropriate odor tag and odor intensity as odor notes are detected during the run.

Sampling and Sample Preparation. Solid-phase microextraction (SPME) utilizing a 1 cm Carboxen-modified PDMS 85 μm fiber (Supelco, Bellefonte, PA) was the primary field and headspace sampling technique utilized for this overview odor profiling study (*14*). The Carboxen−PDMS coating is capable of extracting a wide range of volatile and semivolatile compounds that are relevant to odor (*15*−*17*). SPME collections were carried out under a number of different conditions, including (a) direct sampling of the feedyard and swine barn air, utilizing variations in downwind distance and exposure time for cross-comparison purposes and (b) indirect sampling of the feedyard environment-exposed materials collected in the field and then enclosed in 0.946L (1 qt) glass headspace vessels, utilizing variations in exposure time for cross-comparison purposes. All SPME air-sampling events were carried out under ambient conditions. The collection of field air samples by SPME was conducted at 1 m height using a modified Advanced Pole System (from Wild Birds Unlimited, Round Rock, TX) that was easily deployable. After collection, SPME assemblies were wrapped in clean aluminum foil, placed in a cooler, and shipped to the laboratory at Microanalytics. All air samples were analyzed within 72 h of collection. A separate series of experiments were conducted to determine sample recoveries from Carboxen−PDMS SPME fibers (*17*). Average sample recoveries were 98.3% (±18.6%) for 11 odorous compounds studied including volatile fatty acids (VFAs) ranging from acetic to hexanoic, indole, skatole, *p*-cresol, and 2′-aminoacetophenone. Concentrations of H_2S in ambient air were measured side-by-side with SPME sampling using factory-calibrated Jerome 631-X H_2S monitors (Arizona Instruments, Tempe, AZ).

Confined Animal Feeding Operations. The air environments associated with two different high-density livestock operations were sampled for the purpose of this initial odor profile study series, including a 50000-head-capacity commercial cattle feedyard and a mechanically

Table 1. Environmental Conditions and Measured H_2S Concentrations during Field Air Sampling[a]

location	start	end	H_2S (ppb)	odor description	wind speed at 2 m (m/s)	wind speed at 10 m (m/s)	wind direction (deg)	T_{air} (°C)	RH (%)	P (kPa)
exhaust fan at swine finish barn (Dec 8–10, 2003)										
	12 p.m.	12 p.m.	404 (374)	characteristic swine barn odor	n/a	7.35 (3.14)	247 (76)	16.0 (3.90)	52.0 (7.27)	88.0
20 m downwind from commercial cattle feedyard (Jan 28, 2004)										
	10.20 a.m.	2:20 p.m.	3.75 (1.5)	feedyard odor and burnt crop field smell	6.84 (0.47)	9.14 (0.62)	239 (15)	8.95 (2.38)	22.5 (3.11)	88.2 (0.05)
2000 m downwind from commercial cattle feedyard (Jan 28, 2004)										
	11:55 a.m.	3:55 p.m.	3.4 (0.55)	faint feedyard odor and burnt crop field smell	6.25 (0.77)	8.19 (1.14)	251 (9.6)	12.0 (1.71)	19.7 (0.96)	88.1 (0.08)
adsorption to common materials inside a commercial cattle feedyard (Jan 28–Feb 18, 2004)										
	12 p.m.	12 p.m.	n/a	characteristic feedyard odor	3.23 (1.13)	n/a	197 (57)	2.50 (3.60)	n/a	n/a

[a] Values in parentheses signify standard deviation around mean; n/a = not available.

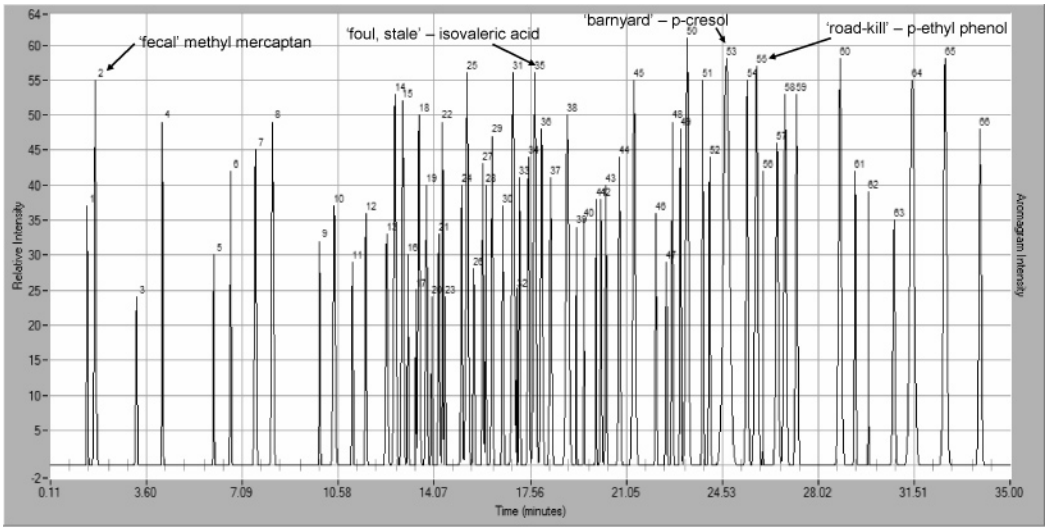

Figure 2. Aromagram from 48 h SPME collection at the exhaust fan of a swine finish barn.

ventilated swine finish barn site (5000-head capacity) in northwestern Texas. In addition, soil samples and materials exposed for extended periods of time in these environments were also collected and analyzed. For downwind air sampling, an attempt was made to limit it to periods of relatively stable wind directions. Meteorological conditions, general odor assessments, and independent measurements of H_2S concentrations were carried out at the start, during, and at the end of the direct SPME sampling periods. In the case of the swine facility, exploratory direct SPME headspace samples were collected from both inside and outside the barns. **Table 1** summarizes the environmental conditions and side-by-side H_2S measurements during field events in this study.

RESULTS AND DISCUSSION

The odor profiling investigative process was basically identical to the one we use to define the major odor carriers in a plastic-packaged food product or in a work environment (*7*, *10*−*13*). This process essentially involved sampling and concentrating with SPME and analyzing the volatile odorants directly from the field or target headspace, ranking the individual odorants relative to odor character and intensity, and correlating to a sensory panel gradation of the composite sampled environment. This process was carried out under a variety of conditions relative to the commercial cattle feedyard and a swine barn in northwestern Texas. These efforts, as summarized below, reconfirm (i.e., as previously reported in refs *2*−*6* and *9*) the overall complexity of these environments, in terms of both total volatile compounds emitted and the number of significant potential odorants among those volatile compounds.

Aromagram of Swine Finish Barn Odor. In the examples that follow, the interpretation of the term "aromagram" is simply a graphical representation of aroma or odor intensity and characterization for chromatographically separated individual odorants from a complex matrix. An aromagram from a 48 h SPME collection at the exhaust fan of a swine finish barn is presented in **Figure 2**. This aromagram was generated by the GC-O investigator monitoring the odor impact of the individual compounds as they elute from the chromatographic column. The retention time span of the peaks reflects the start and end time for the individual odor responses, whereas the peak height reflects the perceived relative intensity of these responses. For a single, discrete GC-O profile run the initial responses are simply intensity approximation assessments "relative" to the baseline (i.e., the absence of a particular odor response). With respect to a series of related profiles, incorporating variations in odorant loadings, the responses can take on the added dimension of intensity response approximations relative to a dilution series. By overlaying these sensory responses with the PID and MS signals, it was possible to correlate the sensory responses with corresponding electronic signals and odorant identification, respectively. At least 66 discrete odor notes were detected under the conditions of collection, and many of these reflected intense to overwhelming odor intensities. The full range of previously reported swine farm odorants was detected, including H_2S and its organic homologues; trimethylamine; VFAs ranging from acetic to octanoic; phenolics, including phenol, *p*-cresol, and *p*-ethylphenol; indole, skatole, and a wide variety of ketones, diones, and aldehydes. A summary of a few of the major odorants from this odor profile analysis is presented in **Table 2**.

Effects of Sampling Time and Sampling Location. Among the lessons we have learned using a GC-O-based approach to

Table 2. Representative Odorants from Inside a Tunnel-Ventilated Swine Finish Barn Collected for 48 h with SPME near the Continuous Exhaust Fan

odorant retention time (min)	odor descriptor	preliminary odorant identification
1.42	foul, fecal	hydrogen sulfide
1.68	fecal	methyl mercaptan
1.70	fishy	trimethylamine
4.15	buttery	diacetyl
6.60	amine	unknown amine or diamine
7.60	grassy	hexanal
10.30	buttery	pentanedione
12.60	savory, nutty	dimethylpyrazine
13.45	musty, vinegar	acetic acid
13.85	fecal	dimethyl trisulfide
15.20	vomitus, body odor	propionic acid
15.85	cardboard, musty	? nonenal
16.80	vomitus, body odor	butyric acid
17.60	body odor, foul	isovaleric acid
18.80	foul, characteristic	valeric acid
21.30	medicinal	guaiacol
23.14	medicinal, floral	phenol
24.10	beet, vegetable	geosmin
24.40	barnyard, characteristic	*p*-cresol
25.80	roadkill, decay, foul	*p*-ethylphenol
27.15	taco shell, bat cave	2′-aminoacetophenone
28.70	outhouse	*p*-vinylphenol
29.83	outhouse	indole
30.70	outhouse, naphthalenic	skatole
31.26	floral, honey	phenylacetic acid
32.50	taco shell, bat cave	1-(2-aminophenyl)-1-butanone

malodor investigations is that it is possible to look too closely at the volatiles/odorants composition of any matrix. Utilizing appropriate volatiles concentration techniques it is always possible to generate a "forest" of chromatographic peaks and corresponding odor notes. From a practical standpoint, that is, relative to odor impact at a long distance from the source, most of that data (collected at the source) is little more than background clutter or noise with negligible contribution to the primary sensory gradation difference. An example of this from the current study is shown in **Figure 2**, where a long sampling time of 48 h at the source (barn) was used. The use of long extraction time combined with proximity to the source resulted in overwhelming odor intensities that precluded odor prioritization. Thus, for the purpose of reducing this mass of data and focusing on the most important odorants in the field, it was necessary to adopt a strategy of reduced collection time and/or increasing distance from the odor source. **Figures 3** and **4** reflect such a series and show aromagrams generated at increasing distance (20 and 2000 m) from the commercial beef cattle feedyard source and under shorter collection times, that is, 4 h, relative to that adopted for **Figure 2**. The reduced sample loadings reflected in this pair of aromagrams present a much more useful profile of the key individual odorants within these environments. Key observations that can be extracted from this sample series are the following:

- Increasing distance from the source results in a significant reduction in the total number of detectable odors as well as corresponding reductions in odor impact intensities for those odors that are detectable. Most noteworthy is the fact that, of the most commonly cited feedyard odorants, only *p*-cresol was shown to carry a significant individual olfactory response for the ~2000 m distance sample. Although the olfactory response for *p*-cresol was shown to be reduced by ~50% relative to the near-site equivalent at 20 m (**Figure 3**), this response was still recordable as "strong" and "characteristic barnyard". In contrast, all other primary focus odorants were shown to be below their respective odor thresholds with the exception of isovaleric acid, which was only faintly detectable.
- The near-site collection (**Figure 3**) resulted in strong-to-intense odor responses for most of the cited cattle feedyard odorants (*2*, *3*, *6*). In our study, particularly prominent was an intense "barnyard", "urinous", or "characteristic" response for *p*-cresol. A second tier of strong to intense responses was shown for *p*-ethylphenol, characterized by "foul" or "roadkill" odor; isovaleric acid ("body odor", "musty" odor); butyric acid ("vomitus" odor); and trimethylamine ("fishy").
- Relative to the near-site collection at 20 m (**Figure 3**), only the dimethyl trisulfide homologue of the sulfide series presented a significant individual odor response (strong "fecal" odor). There were no significant odor responses for H_2S or its lower molecular weight organic homologues. Side-by-side measurements of H_2S concentration at the near-site sampling point (20 m) confirmed that the ~3 ppb of H_2S levels were too far below the published odor threshold of approximately 10 ppb (*8*) to 130 ppb (*18*) to contribute significantly to the strong composite odor perceived at that position and time of sampling (**Table 1**).
- The near-site collection (**Figure 3**) resulted in a surprisingly strong to intense "fishy" odor note corresponding to trimethylamine. This strong response is particularly noteworthy considering the aforementioned absence, in this chromatographic region, of odor responses for H_2S, methyl mercaptan, or dimethyl sulfide.

Odor Priority Rankings for a Beef Cattle Feedyard. The goal of these odor profile studies was to develop an approximate qualitative priority ranking of the individual odorants as emitted by the source. In the current study there were distinct differences in the odor profiles that existed at (**Figure 3**) or at a distance from the source (**Figure 4**). **Table 3** summarizes the approximate top odor profile rankings for sampling points near and distant from the source as extracted from the odor profile study of the beef cattle feedyard. The top odorants at the near location were trimethylamine, *p*-cresol, and butyric acid, respectively. The top odorants at the distant location were *p*-cresol, isovaleric acid, and *p*-ethylphenol. The distant location is more characteristic of neighbor/receptor locations in this part of Texas. It is noteworthy to mention that *p*-cresol was also the top priority odorant determined for 1 h sampling with SPME during a characteristic beef cattle feedlot odor event in Amarillo, TX, that followed 2−3 days after rain or snow-melting events. This event was characterized by steady southwesterly winds. The nearest beef cattle feedlot was located ~16 km upwind from the sampling site. Thus, *p*-cresol appears to be a good candidate for a compound that could be modeled as a surrogate odor for atmospheric dispersion modeling. It is also likely that the inclusion of chemical reactions of key odorants may be needed to better predict the fate of odor.

A number of factors were taken into consideration in the development of this initial priority ranking profile. These include odor character, detectability, and perceived intensity. Relative to our approach, it can be stated that odor character carries considerably more weight than relative intensity or detectability. It is for this reason that a high impact, "character-defining" odorant may or may not carry the greatest individual odor intensity in an individual or series of GC-O odor profiles. This character-defining aspect of an individual odorant within a complex matrix of secondary odorants is of greatest importance relative to odorant prioritization. Simply stated, if upon composite odor assessment of a material or environment the odor character of an individual odorant is easily discernible from the

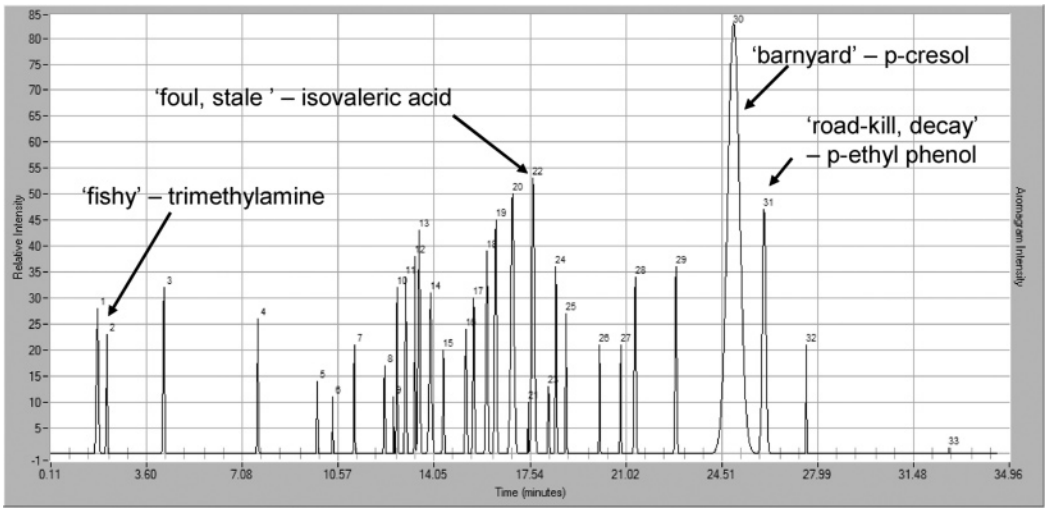

Figure 3. Aromagram for 4 h SPME fiber collection 20 m downwind ("near" site) from commercial beef cattle feedyard.

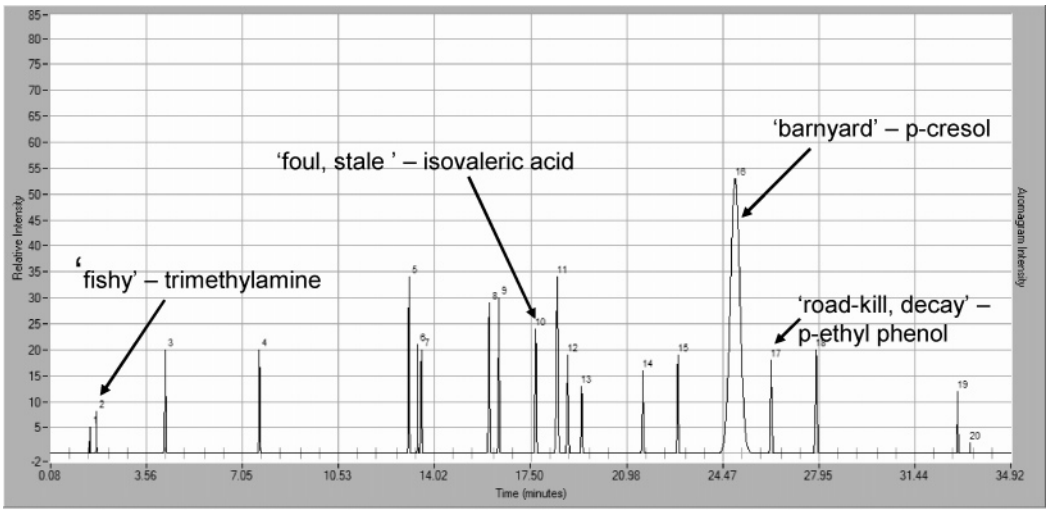

Figure 4. Aromagram for 4 h SPME fiber collection 2000 m downwind ("distant" site) from commercial beef cattle feedyard.

Table 3. Approximate Odor Profile Priority Rankings for a Commercial Cattle Feedyard

odor priority ranking	near source (20 m)	distant from source (2000 m)
1	trimethylamine	*p*-cresol
2	*p*-cresol	isovaleric acid
3	butyric acid	*p*-ethylphenol

complex odorant matrix that accompanies it, that individual odorant has to be considered of greater importance relative to overall odor impact. As an example, despite a relatively complex odorant matrix, the characteristic aroma of beets is defined predominantly by geosmin, a single, extremely potent, character-defining odorant (*19*). However, these results must be interpreted within the context of the characteristics and limitations of the SPME sampling approach. The sensitivity of the SPME technique to solubility constants and volatility-driven sample rate constants is well recognized (*14*) and must be considered relative to these preliminary assessments. In addition, it is well documented that livestock dust is a major carrier of swine odor (*20*, *21*). It was known that selected SPME fiber coatings can extract airborne particles, for example, emitted from diesel engine exhaust (*22*). Thus, it is possible that SPME fibers used in this research collected some livestock or background dust while being exposed to either exhaust air from a swine barn or downwind from a cattle feedlot. Such extractions of dust with SPME are likely to be due to mechanical impaction on the fiber coating. However, the extent of dust contribution to the odor in this study is not known at this time. New comprehensive experiments related to the partitioning of key malodorous compounds and other VOCs to swine particulate matter were completed in the fall of 2004. In these experiments, actual dust concentration measurements at several particle sizes inside a commercial swine finish barn in Iowa were conducted using side-by-side dust analyzers. Gases desorbing from used filters were then sampled and analyzed with a SPME-MD-GC-MS-O system. More than 60 volatile organic compounds (VOCs) were found (*23*). Characteristic partitioning between the fine and coarse dust measured as PM-1, PM-10, and TSP, respectively, was observed for many of the odorants. In addition, it was observed that characteristic swine odorants had a greater relative (i.e., normalized by measured dust mass) mass in fine dust compared to coarse dust. This observation has a significant impact on modeling of odor dispersion. A comprehensive summary of this research is being prepared for peer-reviewed publication. Repetition of the GC-O-based profile assessment with alternative approaches such as sorbent tube or cryogenic concentration will be critical for confirmation of this critical assessment. One research group combined the use of sorbent tubes with thermal desorption−GC-MS-O for the identification and quantification of odorants in a dairy operation in California

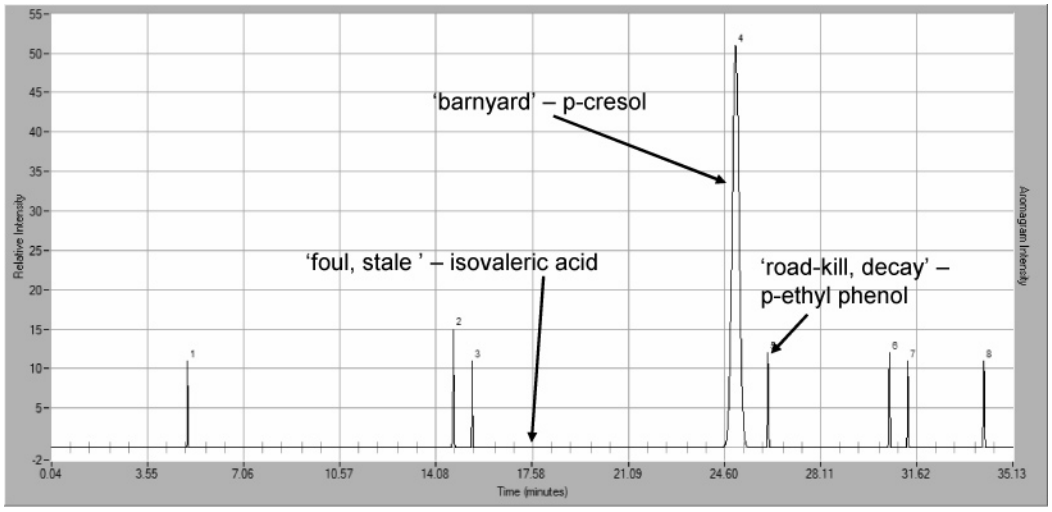

Figure 5. Aromagram for plastic plate exposed for 3 weeks at a large cattle feedyard.

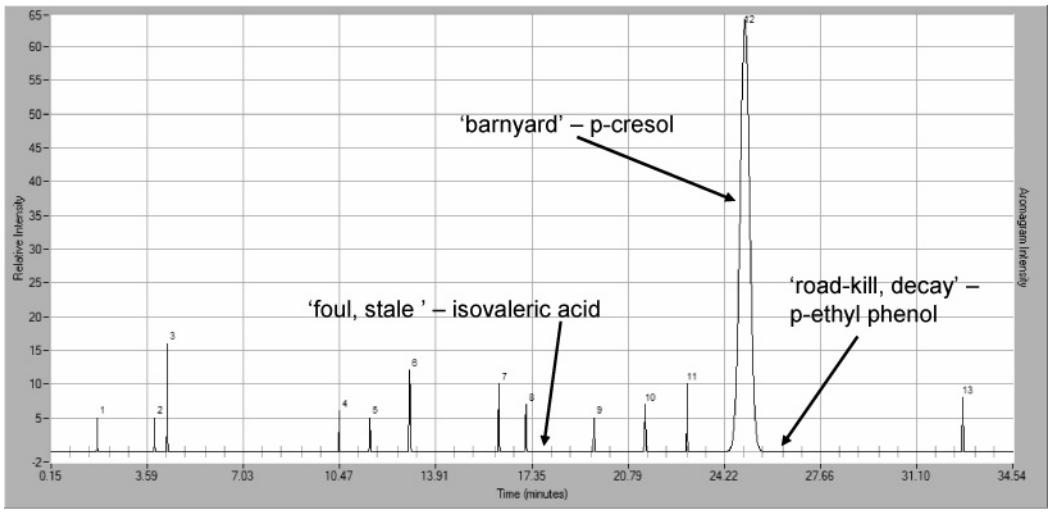

Figure 6. Aromagram for carbon steel plate exposed for 3 weeks at a large cattle feedyard.

(*24*). However, that study reported the absence of many key chemicals or functional groups reported in earlier studies, namely, amines, mercaptans, phenols, cresols, and indoles. The authors suggested possible biases in the method associated with the use of sorbent tubes and capillary column.

Persistence of Key Livestock Odorants in the Environment. A second lesson learned from previous investigations of this type is that special considerations should be made when the key odorants are shown to be compounds of low volatility and high odor potency (e.g., *p*-cresol). Under such conditions these compounds will be slow to diffuse from the source and as a result will tend, over time, to accumulate and increase in concentration at the source, adsorbing onto, permeating into, and reemitting from structural or incidental materials at or near the source. This is analogous to indoor environments where, in extreme cases, it has been necessary to remove structural and incidental materials (i.e., sheetrock, boxes, paper, fiber, and carpet, etc.) from these source areas for effective site odor remediation, because even forced ventilation effects can be too slow under these conditions. **Figures 5** and **6** below illustrate this effect relative to two types of material specimens (10 × 5 × 0.6 cm plates) that were exposed to air inside a 50000-head cattle feedyard for 3 weeks. Samples were collected from closed headspace of clean jars holding these specimens after a 3 week collection period.

A significant consideration relative to these odor profiles is the fact that the environment-exposed specimens were thoroughly flushed with tap water and blotted dry prior to insertion into clean headspace vessels for sampling. It is noteworthy that despite this prewash sample preparation step to remove particulate matter, a very strong response for *p*-cresol was still detected, even with relatively short sample collection periods. Although this effect was expected for the plastic chip specimen, it was somewhat surprising that it also appeared to hold for the steel plate equivalent. Also noteworthy relative to this sampling series is the fact that, for both plastic and steel, the other commonly targeted odorants were not detected under conditions where the *p*-cresol response was very strong. The tendency for *p*-cresol to tenaciously adsorb onto surfaces may account for a tendency to increase in concentration at the source over time, thereby also increasing the odor impact of the source over time.

Effects of Sample Preparation on Odor. Figures 7 and **8** illustrate another interesting analytical effect that may have practical significance to the field of livestock odor analysis. It is the "flooding out" effect, which is often utilized to increase the headspace concentration of target volatile organics, including the trace level odorants. The addition of an excess of water to a dry solid sample matrix has the effect of displacing adsorbed organics and, in the case of volatile compounds, increasing their relative concentration in the headspace.

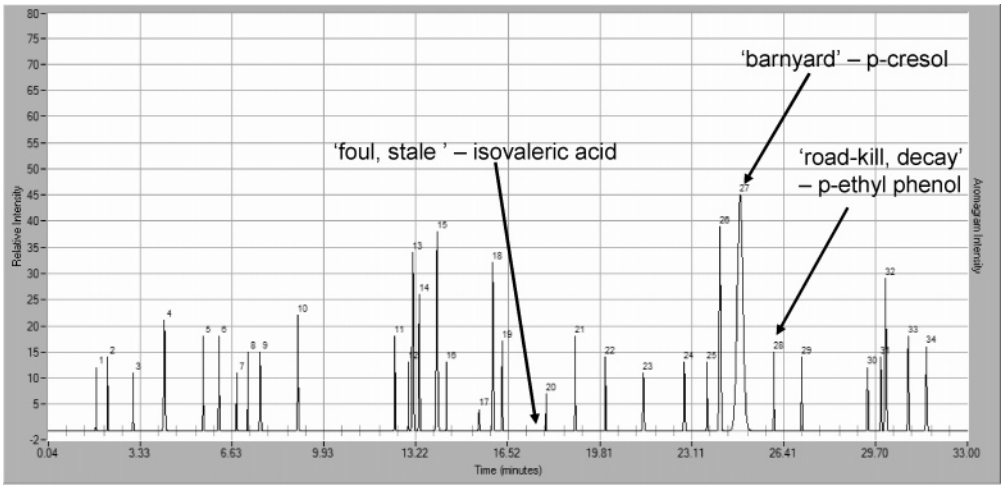

Figure 7. Aromagram for top 3 cm of surface soil taken 50 m downwind from a commercial feedyard. Sample was collected using 1.5 h SPME fiber collection before water was added.

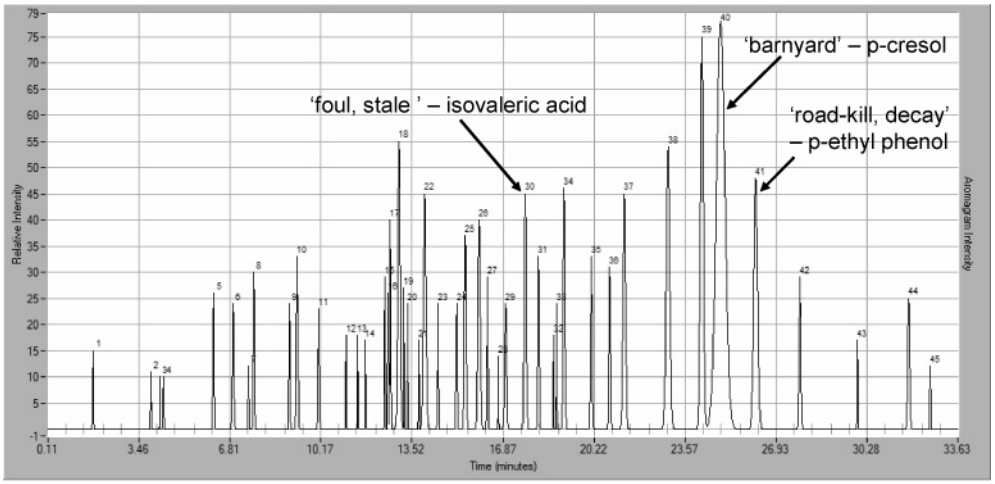

Figure 8. Aromagram for top 3 cm of surface soil taken 50 m downwind from a commercial feedyard. Sample was collected using 1.5 h SPME fiber collection after water added.

These two aromagrams illustrate this flooding out effect relative to a sample of surface soil (i.e., ~top 3 cm) collected 50 m downwind of the same commercial cattle feedyard. **Figure 7** is the aromagram that was generated for the sample as originally submitted, whereas **Figure 8** was generated from the same sample after water saturation. Shown is a dramatic increase in the odorant composition of the sample headspace in terms of both the numbers and relative intensities of the individual odorants. Key observations that can be extracted from this sample series are the following:

- Significant increases are seen relative to several key odorant compounds including peak 40 (*p*-cresol—"barnyard", "characteristic"); peak 41 (*p*-ethylphenol—"foul", "roadkill"); peak 38 (unknown—"musty"); peak 39 (geosmin—"beet", "vegetable"); peak 30 (isovaleric acid—"musty", "body odor"); peak 22 (dimethyl trisulfide—"fecal"), and others. The peak numbers referenced are taken from the postflood aromagram (i.e., **Figure 8**).
- Detectable, but relatively insignificant, responses are found for the lower molecular weight VFAs (i.e., peak 24, propanoic acid; and peak 29, butyric acid). Acetic acid was not odor detectable for either sampled condition.

It is this flooding-out effect that likely accounts for part of the reported increased odor complaints surrounding commercial cattle feedlots after rain events. It is possible, although unproven at this point, that extended periods of dry weather followed by a rain event may magnify the odor impact of this flooding out effect. Another likely reason is the change of biological activity in the manure crust following the addition of water.

Odor Priority Rankings for a Swine Finish Operation. In an effort to develop a more direct comparison of odor profile characteristics between high-density swine and cattle facilities a distance dilution SPME sampling series was carried out downwind from a 5400 head swine finish facility in Texas. **Figures 9** and **10** reflect such a series with aromagrams generated at increasing distance from the experimental facility utilizing shorter collection times (i.e., 20 min) relative to that adopted for **Figures 3** and **4**.

The natural dilution effect that was previously shown (**Figures 3** and **4**) for increasing distance from the beef cattle feedlot is demonstrated, in like manner, for the current swine series. Key qualitative assessments that can be extracted from this aromagram series are the following:

- Increasing distance from the source resulted in a significant reduction in the total number of detectable odors as well as corresponding reductions in odor impact intensities for those odors that were detectable. As was shown relative to the previous cattle feedlot series, only *p*-cresol (peak 11) was shown to carry a significant individual olfactory response for the distance sample (i.e., 250 m). Although the olfactory response

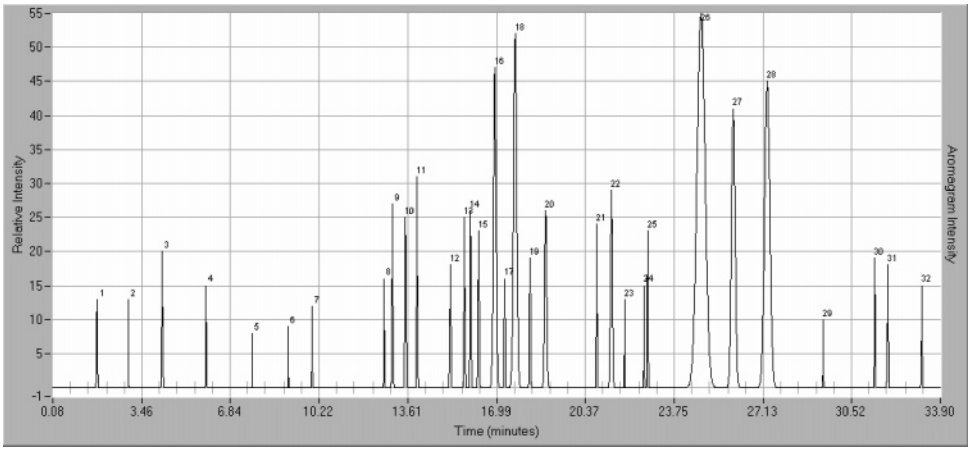

Figure 9. Aromagram for 20 min SPME fiber collection 0.5 m downwind (source) from a swine barn exhaust fan.

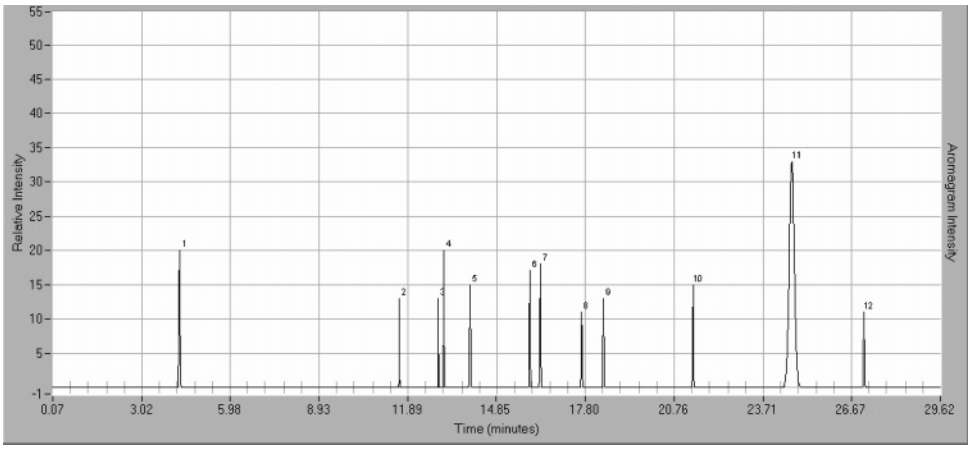

Figure 10. Aromagram for 20 min SPME fiber collection 250 m downwind (distance) from a swine finish operation.

for *p*-cresol was shown to be reduced by ~66% relative to the at-source equivalent (peak 26), this response was still recordable as "distinct to strong" and "characteristic barnyard". In contrast, all other primary focus odorants were shown to be below their respective odor thresholds with the exception of isovaleric acid and 2′-aminoacetophenone, which were only faintly detectable.

• As was shown for the previous cattle feedlot series (**Figures 3** and **4**), *p*-cresol appears to be the single most important individual odorant relative to this swine facility series. However, as summarized in the following paragraphs, when the odor profile results for these two facilities were compared, there also appeared to be differences in relative responses among the major individual odorants. Our high prioritization of *p*-cresol in swine production environments is consistent with an earlier European study published in the 1980s pointing specifically to *p*-cresol and VFAs as the key odorants in swine environments (*25*).

• In contrast to the equivalent near-source cattle feedlot series, this swine facility series presented surprisingly low individual odor impact responses for the odorants of greatest volatility (i.e., trimethylamine, methyl mercaptan, hydrogen sulfide, and dimethyl sulfide). This was in marked contrast to the "strong" to "intense" individual odor responses for the odorants of lower volatility (i.e., butyric acid, isovaleric acid, *p*-cresol, *p*-ethylphenol, and 2′-aminoacetophenone). This bias in odor prominence relative to the odorants of lower volatility potentially takes on greater significance when considered in relation to a well-known characteristic of SPME sampling, that is, a natural bias imposed by short sample collection times which favors the compounds of greater volatility (*26*, *27*). In most cases, compounds with higher volatility that are typically associated with low molecular weight and high vapor pressure will reach equilibrium with SPME coatings more quickly relative to semivolatiles (*14*).

• Taking this factor into account relative to the recent swine facility series, the relative odor impact prominence of the odorants of lowest volatility potentially takes on even greater significance as a result of the relatively short collection times (i.e., 20 min for the recent swine series in contrast to the 1 and 4 h collection times utilized for the previous cattle and swine facility samplings). This effect is presented only as conjecture at this point and will require a more rigorous evaluation to confirm or disprove.

• There appeared to be a rise in relative individual odor prominence for 2′-aminoacetophenone and dimethyl trisulfide relative to the previous cattle series. This rise in significance appeared to coincide with a corresponding reduction in the relative prominence for *p*-ethylphenol.

• There appeared to be a reduction in relative individual odor prominence for indole and skatole relative to the previous (48 h) swine facility collections. Whereas previous swine facility samplings (i.e., both near the source and distant) presented distinct individual responses for these two odorants, the current swine series failed to do so. The reason for this difference is unclear, at this point, but is possibly related to the SPME short sample collection time bias, which was referenced above. As stated previously, this possible explanation is presented only as conjecture at this point and will require a more rigorous evaluation to confirm or disprove.

• Relative to the near-site collection, only the dimethyl trisulfide homologue of the sulfide series presented a significant

Table 4. Approximate Odor Profile Priority Rankings for a Swine Finish Operation

odor priority ranking	near source (0.5 m)	distant from source (250 m)
1	*p*-cresol	*p*-cresol
2	2′-aminoacetophenone	2′-aminoacetophenone
3	isovaleric acid	*p*-ethylphenol

Table 5. Comparison of High Molecular Weight Odorant Ratios—Beef Cattle Feedyard versus Swine Barn

	swine finish barn exhaust	beef cattle feedyard	beef cattle feedyard
distance from source (m)	10	20	20
collection time (h)	1	4	24
p-cresol peak area (ion 107)	526,290	394,769	1,055,076
indole peak area (ion 117)	3157	405	506
skatole peak area (ion 130)	4673	<100	<100
ratio *p*-cresol/indole	~170:1	~1000:1	~2000:1
ratio *p*-cresol/skatole	~110:1	>4000:1	>10500:1

individual odor response (i.e., distinct "fecal"). There were no significant odor responses for H_2S or the lower molecular weight organic homologues (i.e., methyl mercaptan and dimethyl sulfide).

On the basis of the results of this preliminary swine facility odor profile series, the following is presented as an initial odorant prioritization ranking list. As was previously presented for the cattle feedlot distance dilution series, **Table 4** summarizes the approximate top odor profile rankings for near and distant downwind points relative to the recent swine facility profile series.

Ranking of *p*-Cresol. On the basis of this preliminary odor profile survey study, *p*-cresol appeared to constitute the single most prominent odorant emission from both cattle feedyard and confined barn swine operation samples. However, there also appeared to be significant differences between these two sampled environments relative to some of the secondary odorants. This is illustrated in **Table 5** relative to indole and skatole, two other relatively high-boiling odorants that have been previously identified in commercial livestock environments (*9*).

Comparison of the ratio values for the 1 h swine barn vent and 4 h feedlot samples indicated higher swine house vent concentration levels of both indole and skatole relative to *p*-cresol. Although these odor profile experiments were not approached as a rigorous cross-comparison of these two environments, these results are believed to be sufficiently dramatic and consistent to warrant further investigation. Shown to be consistent across a wider cross section of commercial facilities, such ratio differences between primary and secondary odorants can explain perceived odor character differences between different types of operations (*28*).

Previous efforts have shown that although the list of potential odorants may be very similar between animal species in high-density settings, there may be relatively dramatic differences between them regarding the designation of primary and secondary odorant status and corresponding concentration ratios. On the basis of the current odor profile effort, *p*-cresol appears to be the key odor character defining compound relative to distance separation from either the swine finish or beef cattle operation in Texas. The results presented in this paper are focused on the presentation of the SPME-GC-MS-O approach for the identification of key odorants downwind from a cattle feedlot and a swine finish barn. The ranking of specific key odorants was characteristic for the sites that were chosen for this study. In general, many factors can affect aerial emissions of odor, gases, and dust from livestock operations (e.g., size and housing type, waste management system, diet, seasonal and climatic variations, time of day, animal activity). Thus, it is possible that the particular ranking of the most important odorants can vary from site to site. However, it is reasonable to assume that the pool of key odorants used for ranking of specific types of livestock and poultry operations is known.

In summary, these current collaborative efforts were directed at applying to high-density livestock operations some of the lessons learned in utilizing GC-O to resolve past, highly diverse odor-focused investigations in the consumer product industry. Past experience has proven GC-O-based odor profiling to be an essential technology for prioritizing the individual odor contributors to any malodor issue. The prioritization of the individual odor contributors has proven, in turn, to be an essential element of rapid response to crisis-driven malodor issues. On the basis of these current overview odor profile efforts, *p*-cresol appears to be the key odor character defining compound relative to distance separation from the target beef cattle feedyard and swine finish facilities in Texas. As expected, at or near-source odor profiles were much more complex, with the full range of previously reported livestock odorants detected, including hydrogen sulfide and its organic homologues, trimethylamine, and VFAs, ranging from acetic to octanoic. However, a surprising odor impact prominence for trimethylamine was shown for the near-source beef cattle feedyard. If these priority rankings can be proven to be consistent across a broader sampling of similar environments, it will be essential that sampling, analytical, and odor abatement strategies be developed or modified to reflect these priority rankings (*11*). Particular attention appears to be warranted for *p*-cresol due to several factors, including the following:

- odor impact prominence over great distances from the source;
- relatively low volatility and high polarity, factors that may result in slow diffusion and at-source concentration buildup over time;
- surface adsorption propensity and "stickiness", which may magnify the near-source concentration buildup and odor impact effect through adsorption, permeation, and re-emission effects from organic, structural, or incidental materials at or near the source; and
- sensitivity to the flooding out effect in concert with the above-defined volatility, polarity, and surface adsorption factors, which may serve to induce or magnify weather-related odor excursions.

The observations presented above do not purport to represent a definitive qualitative assessment of the complex field of high-density livestock odor impact. However, these observations are believed to be sufficiently compelling to warrant a more comprehensive GC-O-based odor profiling investigation.

SAFETY

Industry biosecurity protocols were followed during field air sampling at the beef cattle feedlot and the swine finish operation. Short extractions of vapors of pure standards with SPME were conducted in vented hoods using gloves.

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